Emerging "new" Brominated flame retardants: Sources and Transport

Dorte Herzke[1], Mikael Harju[1] Eldbjørg Heimstad[1,] Torkjel Sandanger [1], Stefan Posner[2], Frank Wania[3]
1 Norwegian Institute for Air Research, Norway
2 SWEREA; Sweden
3 Department of Physical and Environmental Sciences, University of Toronto at Scarborough; Canada

Introduction

Several types of halogenated organic flame retardants, mainly brominated flame retardants, are described in the literature. This includes compounds belonging to the families of polybrominated diphenylethers (PBDEs), tetrabromobisphenol-A (TBBPA) and its derivatives, such as tetrabromobisphenol A bis(dibromopropyl ether) and tetrabromobisphenol A bis (allyl ether), tribromophenol (TBP) and brominated phthalic anhydride. Use of flame retardant additives depends mainly on the type of polymer to be flame retarded. Although the use of halogenated flame retardants is under increasing scrutiny due to their potentially harmful environmental and health characteristics they represent around 25% by volume of the total global production of flame retardants with a growth of around 5% per year (SRI consulting, 2008). Over the past 30 years PBDEs and TBBP A have been the focus of environmental research determining the characteristics and fate of these compounds. In response to recent regulations on the use of some BFRs, new brominated derivates are being introduced by industry and emitted into the environment. Little is known about the fate and long-range transport capabilities of non-PBDE BFRs. In a report for the Norwegian Climate and Pollution Agency, we assessed sources, transport and fate of emerging BFRs (Harju et al., 2009).

Method

The production volumes for the non-PBDE BFRs were estimated based on known production volumes for TBBP-A, HBCD and PBDEs. Accessible literature and databases were reviewed in order to assess the areas of industrial applications and use of new emerging BFRs. The potential for long range transport (LRT) is one of the criteria for defining a compound as a persistent organic pollutant (POP). The long range transport potential of 21 selected non-PBDE brominated flame retardants was estimated using model-based tools that are well established and readily available.

Results and Discussion

Current production volumes for these BFRs are largely unknown and most data available is outdated. The total global use of brominated flame retardants consisted of 410 000 metric tonnes in 2008. TBBPA, decaBDE and HBCD represent the most commonly used BFRs worldwide, with about 230 000, 73 000, and 21 000 metric tons (SRI consulting, 2008), respectively. If we assume that the production volumes of TBBP-A and decaBDE have not changed dramatically over the past few years, other BFRs are produced and used in volumes of approximately 86 000 metric tons per year, possibly also including BFRs other than those included in this study. The investigated BFRs are used as additives (ethylene bistetrabromo phthalimide, pentabromoethylbenzene), reactive intermediates (dibromoneopentyl glycol) and reactives (2,4,6-tribromophenyl allyl ether) in a wide range of polymers. Possible applications for the treated polymers are in electronics, transportation, circuit boards, coatings, cushioning materials, packaging and padding. Little is known about the produced amounts of the new BFRs but they belong mostly to the category of low volume production.

The potential for these selected BFRs to be subjected to long range transport (LRT) was studied. Dibrominated styrenes (CAS 31780-26-4, 125904-11-2), 2,4,6-tribromophenyl allyl ether (CAS 3278-89-5) and pentabromobenzyl acrylate (CAS 59447-55-1) - based on their partitioning properties alone - were judged to have the potential to undergo LRT. However, estimated short atmospheric half-life indicates that they are more likely to pose a problem in the near source environment, especially if they should be recalcitrant to biotransformation. A valid concern is whether pentabromobenzyl acrylate may form a persistent and potentially bioaccumulative metabolite.

The substances that have partitioning properties that suggests LRT and are predicted to be fairly persistent are the highly brominated monoaromatics, such as hexabromobenzene, pentabromotoluene, and pentabromoethylbenzene. The predicted LRT behaviour is comparable to those of established POPs, although these predictions may be overestimated because the LRT assessment and degradation tool (EPISuite) does not include the possibility of photolytic debromination. Some of the heavier BFRs, such as decabromodiphenylethane (CAS 84852-53-9), have structure similarities todecaBDE, and may be subject to similar long range transport, degradation and bioaccumulation processes.

The likely LRT behaviour of the "new" BFR using only chemical distribution properties, i.e. ignoring the persistence of the compounds, was investigated. We used the air-water partitioning coefficient K_{AW} and the octanol-air partitioning coefficient K_{OA} to locate the BFR chemicals in the chemical partitioning space defined by these two equilibrium partitioning coefficients. K_{AW} and K_{OA} were predicted with the SPARC On-line Calculator, which is a chemical property prediction software, available for public use, free of charge, and can be accessed at http://sparc.chem.uga.edu.

Table 1. Partitioning properties

CAS	Name	log K_{OA}	log K_{AW}
36483-57-5	1-Propanol, 2,2-dimethyl-, tribromo deriv.[a]	7.1	-4.28
1522-92-5	Tribromoneopentyl alcohola	7.6	-5.69
125904-11-2*	1,4 dibromo-2 ethynyl benzene (Dibromostyrene der.).[a]	6.4	-1.90
31780-26-4	2,2-dibromoethenylbenzene (Dibromostyrene der.)[a]	6.2	-1.62
2039-88-5	Benzene, 1-bromo-2-ethenyl (Monobromostyrene der)[a]	5.1	-1.38
118-79-6	2,4,6-Tribromophenol	6.6	-2.30
19186-97-1	Tris(tribromoneopentyl) phosphate	15.0	-6.08
20566-35-2 or 77098-07-8	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-2-(2-hydroxyethoxy)ethyl 2-hydroxypropyl ester	18.8	-14.49
21850-44-2	Tetrabromobisphenol A bis(2,3-dibromopropyl ether)	21.0	-8.01
25327-89-3	Tetrabromobisphenol A diallyl ether	15.5	-4.43
26040-51-7	Bis(2-ethylhexyl) tetrabromophthalate	17.7	-5.95
3278-89-5	2,4,6-Tribromophenyl allyl ether	8.2	-2.41
3296-90-0	Dibromoneopentyl glycol	7.5	-7.66
37853-59-1	1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE)	15.0	-5.17
56362017 or 25713-60-4	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5 triazine	24.9	-11.43
58965-66-5 or 32588-76-4	Ethylene bis(tetrabromophthalimide) (EBTPI)	26.7	-9.06
59447-55-1	Pentabromobenzyl acrylate	11.7	-5.24
632-79-1	Tetrabromophtalic anhydride	11.8	-9.04
84852-53-9	Decabromodiphenylethane (DBDPE)	18.8	-6.29
85-22-3	Pentabromoethylbenzene	9.9	-2.92
87-82-1	Hexabromobenzene (HBB)	9.9	-3.03
87-83-2	Pentabromotoluene (PBT)	9.5	-3.00

The software SPARC and SciFinder has identified the following structures and properties for the listed cas.no.

We then used previously published chemical space maps (Figure 1 (Wania, 2003; Wania, 2006; Czub et al., 2008)) that we overlaid with the BFRs to deduce something about their transport behavior.
Using the results of global transport simulations for a number of hypothetical chemical partitioning property combinations, Wania (2003, 2006) defined four modes of global transport behaviour for organic chemicals. These are: **Fliers:** Substances that are too volatile to partition appreciably into the surface compartments water and soil. These substances can have a very high LRT potential if they are resistant to degradation in the atmosphere. However, their high volatility also means that they generally are not bioaccumulating in foodchains. **Multihoppers:** Substances with intermediate volatility that have the potential to cycle between the atmosphere and the Earth's surface by repeated deposition and evaporation. Some exchange primarily with aquatic surface media, others with terrestrial compartments (soil/foliage), and yet others can exchange with all type of surface media. If sufficiently persistent in air and surface media, such substances have a very large potential to accumulate in polar regions. **Single Hoppers:** Substances that are too involatile to re-evaporate after they have been deposited to the Earth's surface. These chemicals can still undergo LRT, if they are emitted into the atmosphere and are not deposited until they reach the remote region (e.g. when rapid atmospheric transport occurs during a period of no precipitation). **Swimmers:** Substances that are water soluble and therefore could undergo LRT in the oceans (and in rivers), if they are very persistent in the aqueous phase. An example of a persistent swimmer is perfluorooctanesulfonate (PFOS). By comparing the estimated partitioning properties of the "new" BFR with the ranges of partitioning properties that define the four modes of global transport behaviour (Figure 2), we can speculate as to their likely transport characteristics.

Based on their partitioning properties five of the investigated BFR substances are likely to be able to readily exchange between the Earth's atmosphere and surface, in particular lakes and oceans (see Figure 2). In other words, they are multi-hoppers (Wania, 2006). These are the styrenes with one or two bromine substitutions (CAS 2039-88-5, 31780-26-4, 125904-11-2), 1,3,5-tribromo-2-(2-propenyloxy)-benzene (CAS 3278-89-5) and 2,4,6-tribromophenol (CAS 118-79-6). We should caution that the partitioning properties of the tribromophenol apply to the protonated form only. The estimated pK_a of 6.34 for this substance however suggests that it can occur in ionized form within the environmentally relevant pH-range, and it will therefore have a considerably lower log K_{AW} value than is indicated in the chemical space maps (indicated by the white arrow pointing downwards).

Three more substances have partitioning properties (log K_{AW} around -3, log K_{OA} around 9.5 to 10) that place them in the transition area between multiple and single hoppers. These are the highly brominated monoaromatic compounds pentabromoethylbenzene (CAS 85-22-3), pentabromotoluene (CAS 87-83-2), and hexabromobenzene (CAS 87-82-1).
Three substances are fairly volatile (log K_{OA} below 8), but due to high water solubility their log K_{AW} is low (log K_{AW} below -4). These are the brominated and hydroxylated neopentyl compounds, whereby the diol (3296-90-0) has a considerably lower log K_{AW} than the mono-alcohols (CAS 36483-57-5 and 1522-92-5). They thus have the partitioning properties enabling transport in the aqueous phase ("swimmers"), i.e. could undergo long range transport in thewater phase, if they are sufficiently resistant to degradation. The tribromophenol (CAS 118-79-6) in its protonated form also is a "swimmer". Two substances have partitioning properties in a transition area, where the transport characteristics are poorly defined. These are pentabromobenzyl acrylate (CAS 59447-55-1) and Tetrabromophthalic anhydride (CAS 632-79-1). Most of the remaining brominated flame retardants (CAS 19186-97-1, 20566-35-2 or 77098-07-8, 21850-44-2, 25327-89-3, 26040-51-7, 37853-59-1, 56362017 or 25713-60-4, 58965-66-5 or 32588-76-4, 84852-53-9) are clearly too involatile (log $K_{OA} > 15$) to be present in the atmospheric gas phase. If they occur in the atmosphere at all, it is likely in the particulate form. The atmospheric transport behaviour of these so-called "single hoppers" is determined by the transport behaviour of the particle to which they sorb.

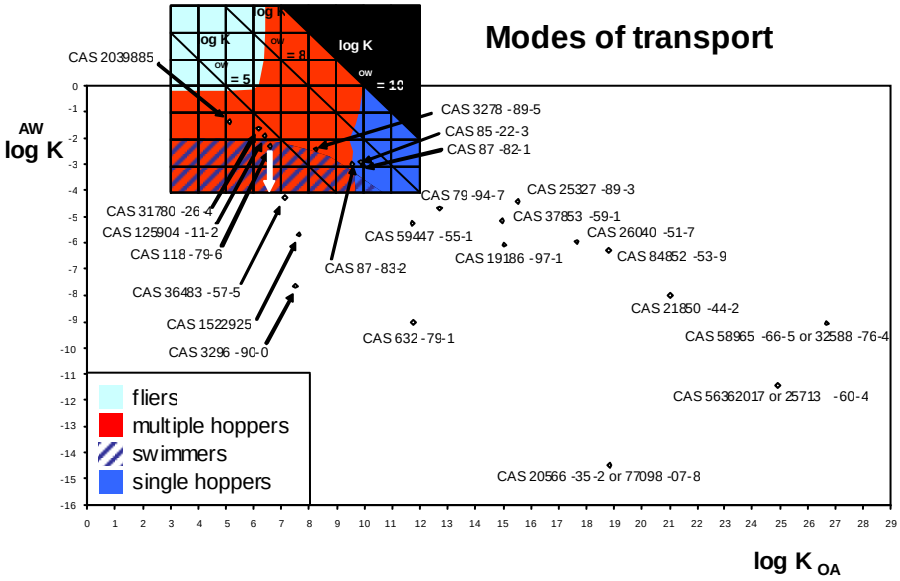

Figure 1. Estimated partitioning properties K_{AW} and K_{OA} of "new" BFR substances relative to the ranges of partitioning properties delineating the four major modes of global transport as established by Wania (2003, 2006). The modes of transport are not indicated for large parts of the chemical space, because no global transport simulations were conducted for substances with log K_{AW} < -4 and log K_{OA} > 12. Substances with log K_{OA} > 12 are likely to be "single hoppers", whereas those with a log K_{AW} < -4 are "swimmers".

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